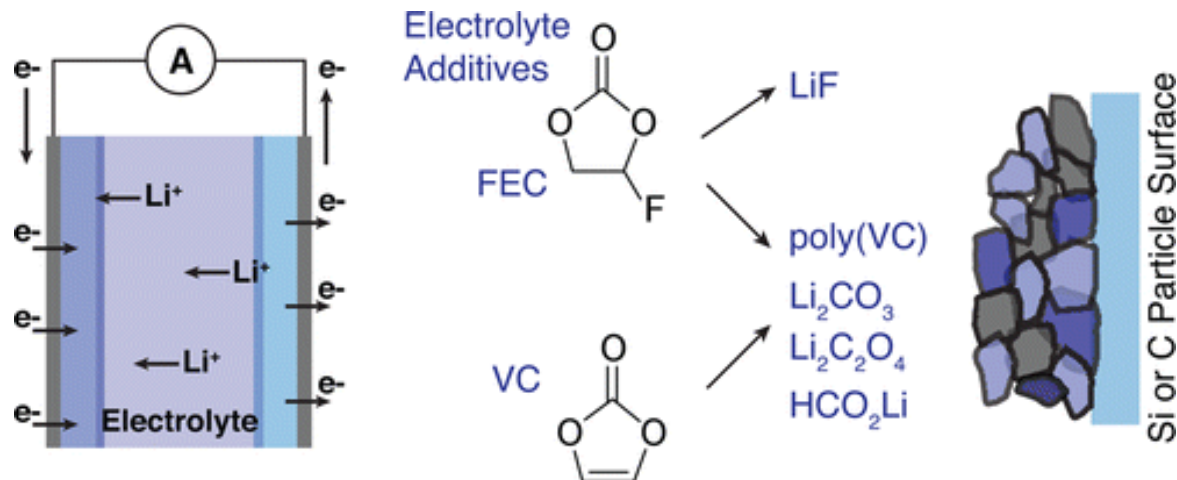


NMR and MRI Studies of SEI, Dendrites, and Electrode Structures

P.I. Name: Clare P. Grey
University of Cambridge

6/7/2017



Project ID
ES055

Overview

Timeline

- Project start date: 10/1/16
- Project end date: 9/30/17
- Percent complete: 80%

Budget

- Funding for FY16: \$275,00 (final year of three year project)
- New project started in FY17 (with same title)
- Funding for FY17: \$275,000

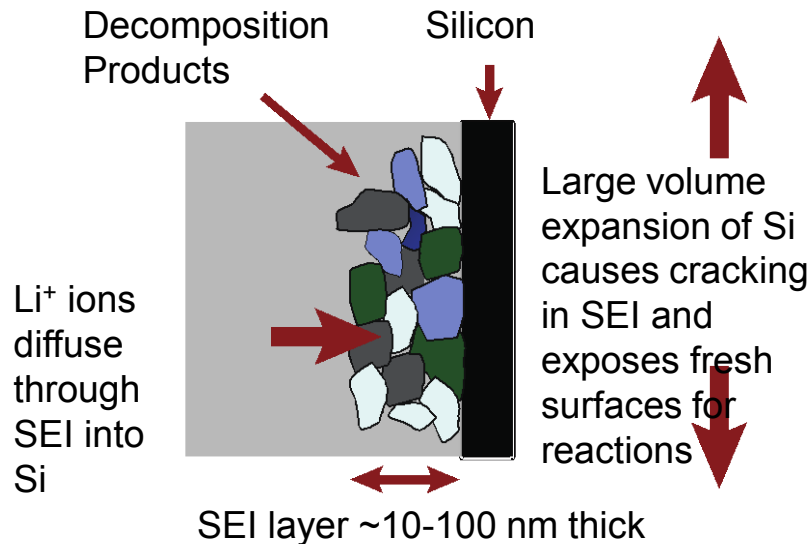


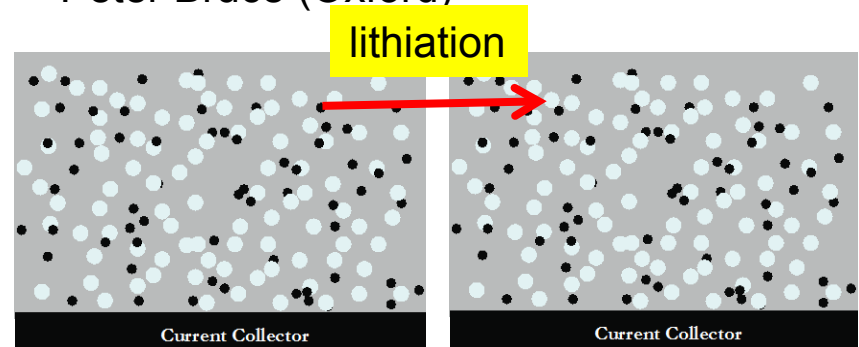
Figure based on E. Peled et al.
J. Electrochem. Soc. 144, L208 (1997)

Barriers

- Life (capacity fade)
- Performance (high energy density)
- Rate

Partners

- Brett Lucht (Rhode Island)
- Alexej Jerschow (NYU)
- Chunmei Ban (NREL)
- Ram Seshadri (UCSB)
- Shirley Meng (UCSD)
- Peter Chupas (ANL)
- Karena Chapman (ANL)
- Stephan Hoffman; Andrew Morris; Dominic Wright; Erika Eiser; Cate Ducati (U. Cam)
- Paul Shearing (UCL)
- Peter Bruce (Oxford)



Relevance

Overall objectives:

- Design a stable SEI
- Reduce overpotential (e.g., interfacial resistance, “structural hysteresis”)
- Optimise performance of Li and Na high capacity anodes and cathodes

Specific Objectives – April 2016-17

- Identify major solid electrolyte interphase (SEI) components on Si, and their spatial proximity, Li⁺ transport through SEI, and how these change with cycling ([capacity fade](#))

To determine the effect of voltage and additives ([FEC](#)) on the composition of the Si SEI

The first objective is to prepare ¹³C enriched FEC for ¹³C NMR multinuclear studies;

- To synthesize and test new inorganic coatings to increase the Coulombic efficiency seen on cycling Si
- Use recently developed in situ NMR/MRI metrologies to investigate Li (and Na dendrite formation), and the role that additives and different electrolytes play in controlling Li(Na) morphology.
- Develop new coatings for Si to reduce SEI formation
- Identify correlations between SEI structure and thickness and Li metal dendrite formation
- To apply methods developed to study lithium anodes to investigate sodium anodes.
- To compare the nature of the SEI formed on Na vs. Li anodes

Milestones

2016

Q2. Establish the difference between extrinsic and P-doped silicon nanowires.

(6/30/16) **Complete – no clear differences, terminate project**

Q3. Complete SEI study of silicon nanoparticles by NMR spectroscopy. **Complete.**

2 papers published. Develop NMR methodology to examine cathode SEI (9/30/16)

Ongoing

Q4. Produce first optimized coating for Si electrode. (12/31/16) **Complete; initial coatings produced**

2017

Q1 Multinuclear NMR studies of SEI coatings on Si with ^{13}C -FEC. **Complete.**

Paper in preparation.

Q2 MRI/dendrite studies of two ionic liquids. **Ongoing; new cell built**

Q3 DNP studies of SEI on Si with different additives (e.g. FEC) and coatings (e.g. phosphazenes). **DNP Experiments for FEC/Si performed; analysis ongoing**

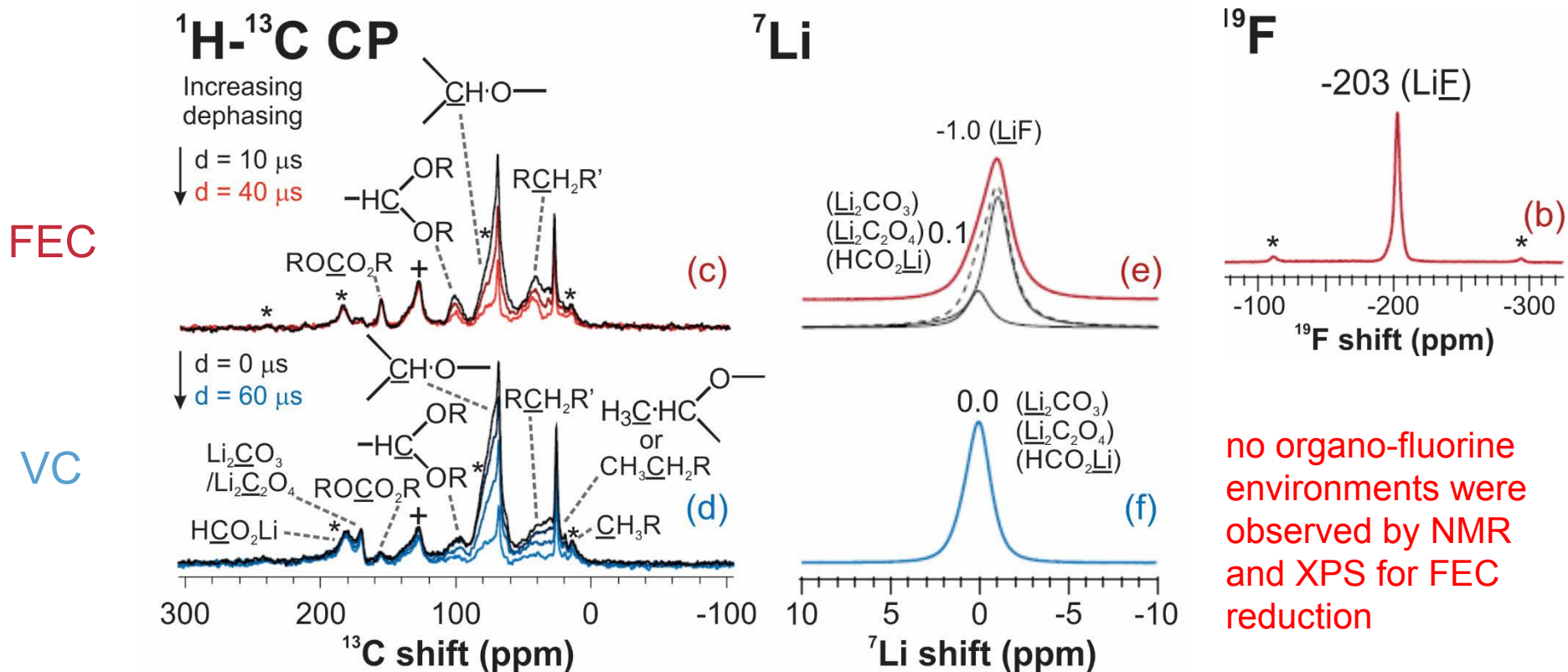
Q4 Multinuclear NMR studies of phase chemistries during (dis)charge of active materials in Na ion batteries. **Cathode work complete; Sn ongoing**

Approach/Strategy

- **Optimizing Si performance**
 - Reduce capacity fade and coulombic inefficiency
 - Reduce overpotential
 - Build a “better” SEI
- **SEI studies**
 - NMR studies of local structure as a function of cycling
 - 2 dimensional and double-resonance NMR studies to establish proximity between species
- **Metal anodes and dendrites**
 - Use spectroscopy and imaging to study mechanisms of dendrite growth
- **Sodium positive and negative electrodes**
 - Contrast LIB and NIB chemistry
- ^{13}C NMR studies of ^{13}C -enriched electrolytes to study SEI organic components; ^7Li , ^{19}F and ^{31}P studies of inorganics.
- Develop DNP methods to study non-enriched electrolytes
- Synthesize enriched FEC and perform NMR studies
- Synthesize decomposition products of FEC and VC via reduction with Li naphthalenide to compare with species present in Si SEI. Carry out multinuclear NMR studies of reduction products (B. Lucht).
- Develop new coating strategies and chemistries (D. Wright, E. Eiser)
- MRI studies to correlate electrolyte concentration gradients with dendrite formation as a function of electrolyte and additives
- Correlate MRI results with X-ray tomography
- Use in-situ methods developed for LIBs to determine the structures of disordered anodes
- Extend NMR studies of paramagnetic cathodes to investigate local structures of NIBs

Technical Accomplishments and Progress

1. Determination of solid products formed on FEC and VC reduction (with B Lucht)

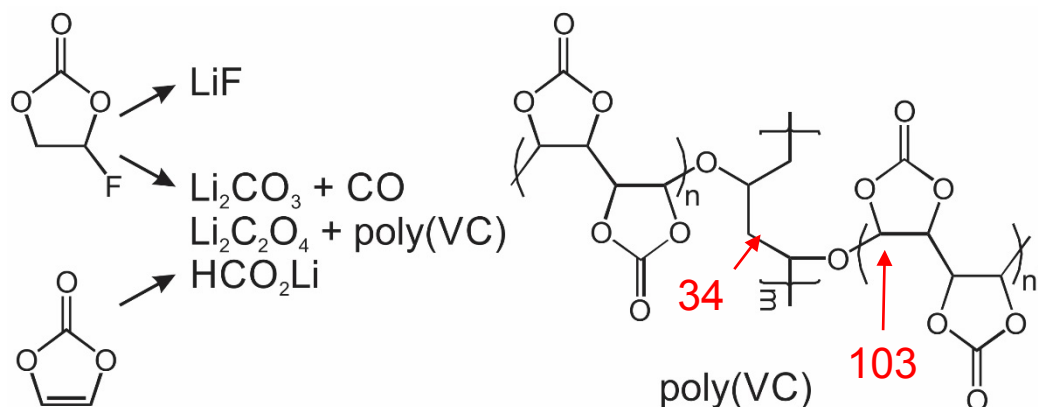


103 ppm resonance not seen in EC SEI studies on Si

Assignments with ^1H , ^{13}C , ^{7}Li , and ^{19}F NMR were supported by FTIR analysis and XPS of FEC/VC reduction products

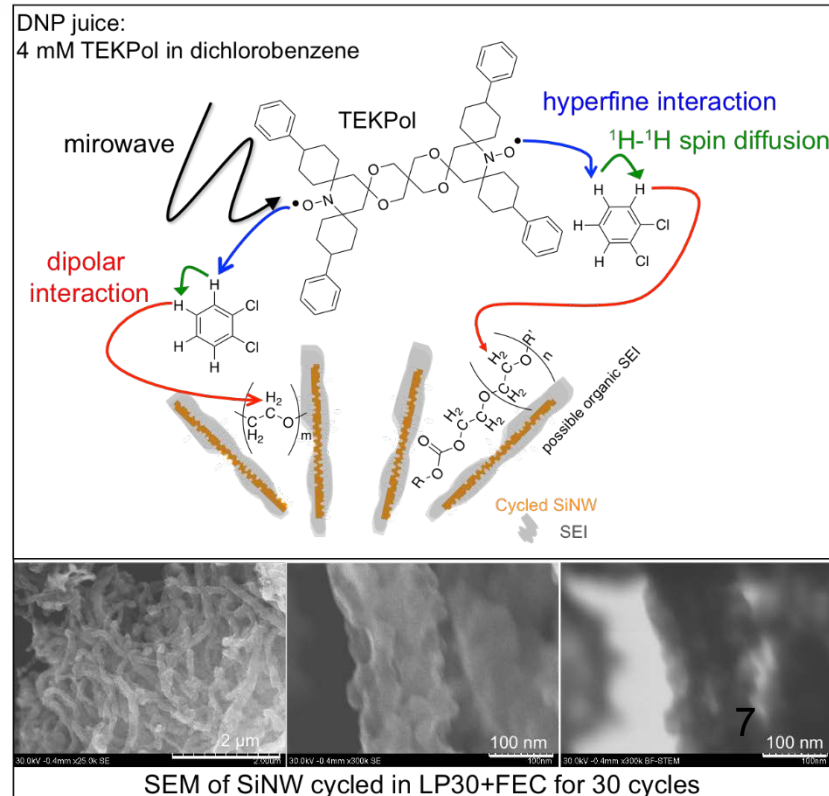
Michan, AL; Parimalam, BS; Leskes, M; Kerber, RN; Yoon, T; Grey, CP; Lucht, BL *Chem. Mater.*, **2016**, 28, 8149.

Proposed FEC/VC reduction products and possible structure for crosslinking site of poly(VC)

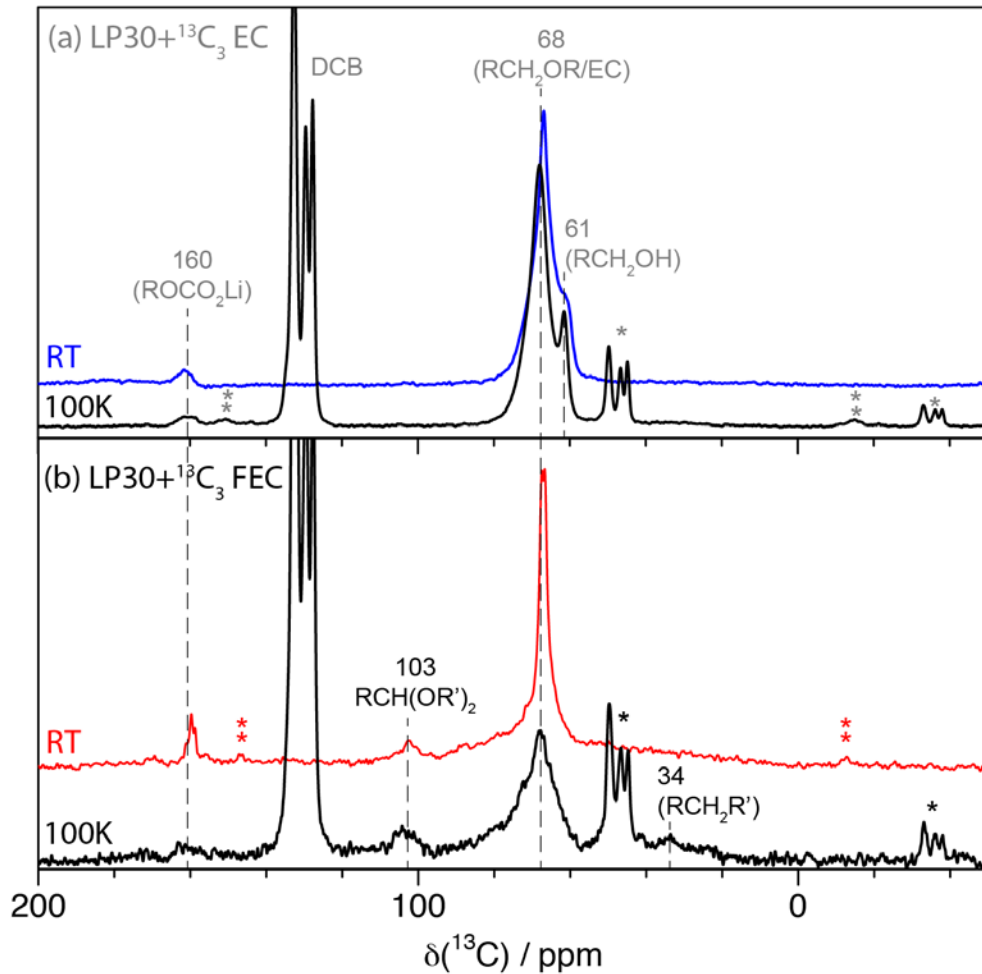


Next steps: use a combination of ^{13}C -labeling and dynamic nuclear polarization (DNP) to probe Si SEI on cycled electrodes

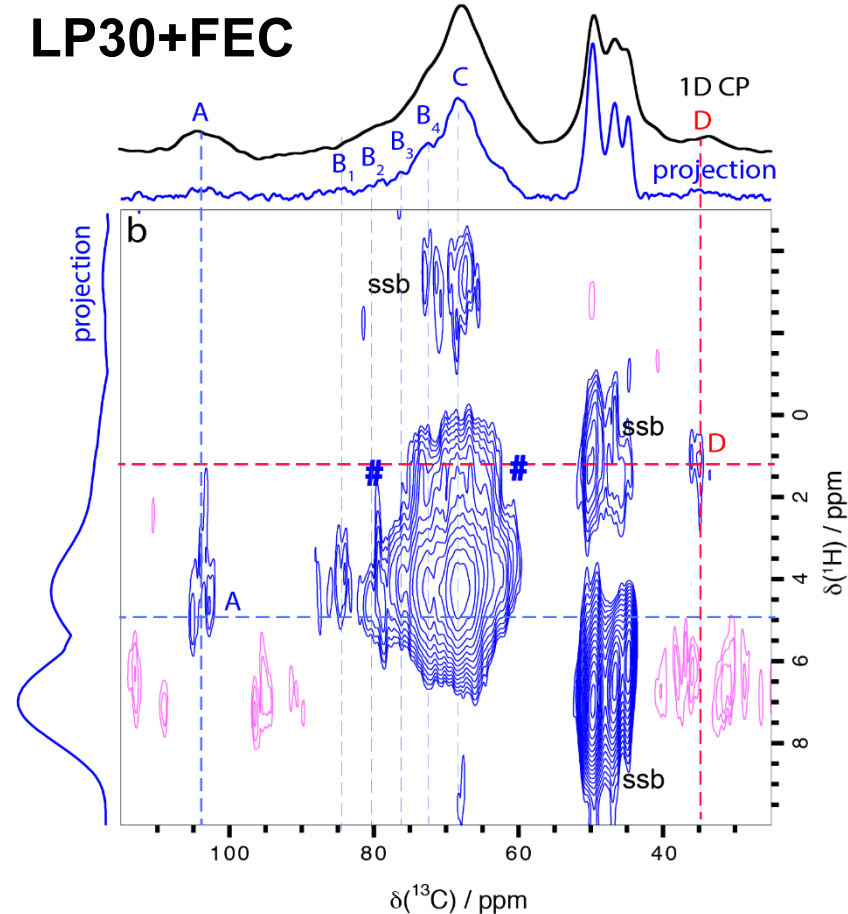
- Use non-enriched electrolytes
- Dichlorobenzene (DCB) used – since its ^{13}C signals do not overlap with main SEI resonances.
- DNP - radical TEKPol – used to create magnetization



Next steps: use a combination of ^{13}C -labeling and DNP to probe Si SEI on cycled electrodes

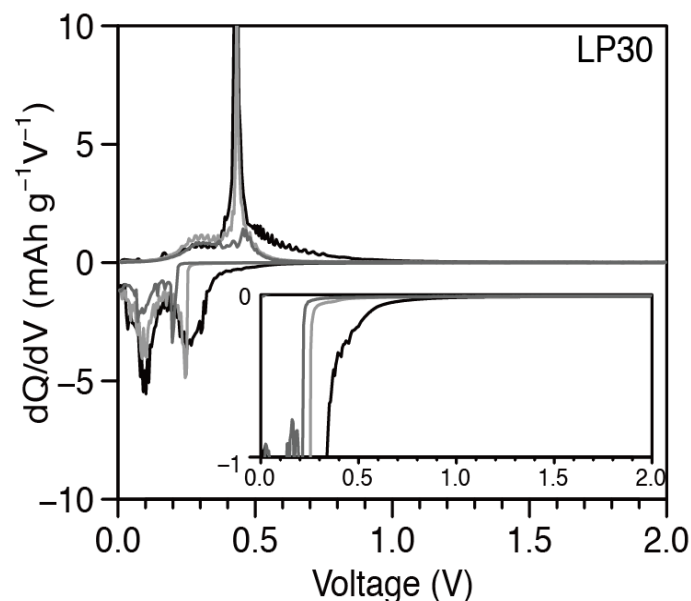
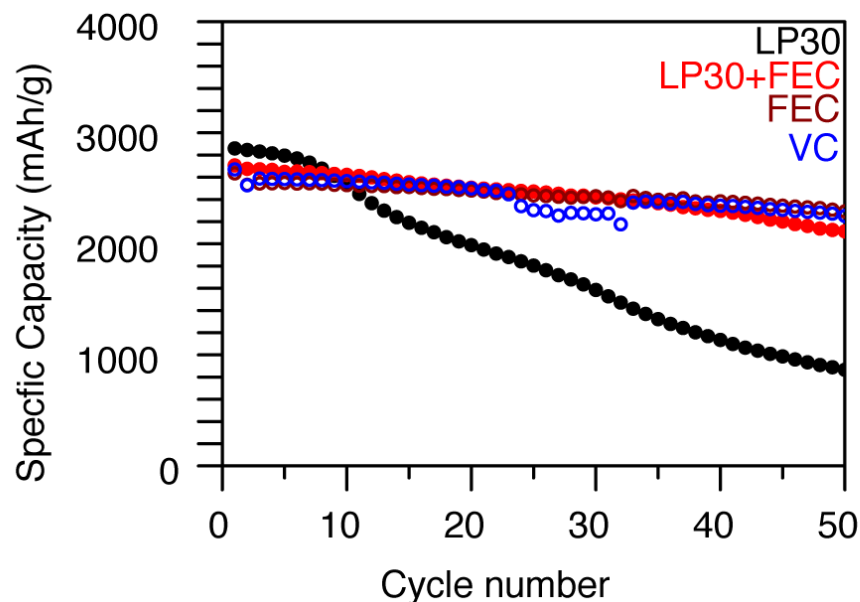


LP30+FEC

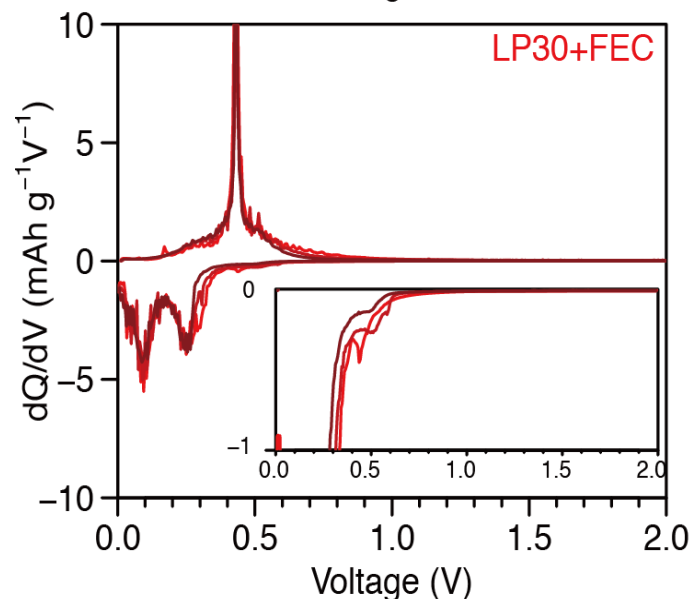
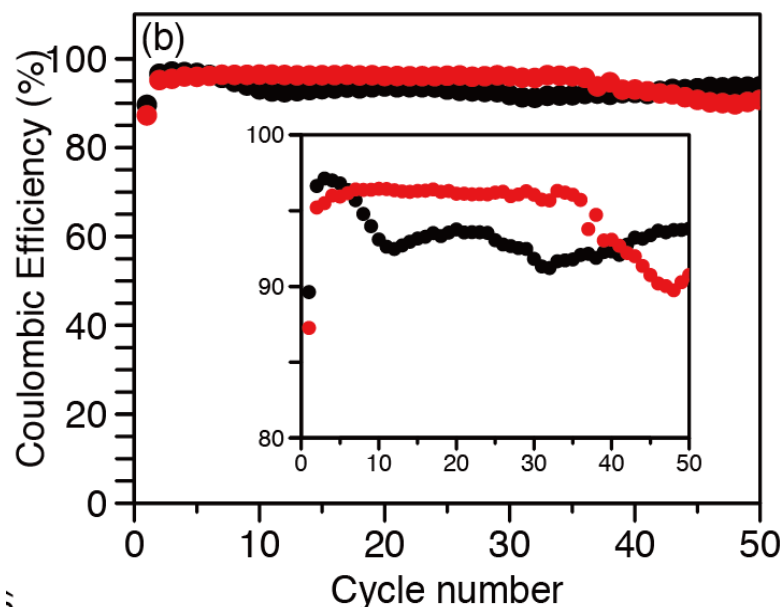


More aliphatics and 103 ppm
“poly-VC” product

Effect of adding FEC and VC additives



10% FEC

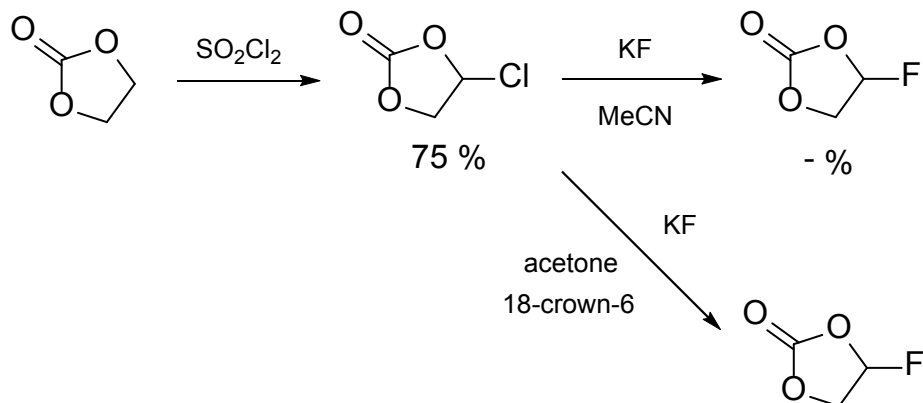


Capacity retention much better but coulombic efficiency is still poor

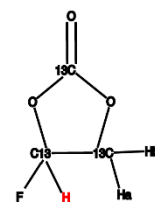
New process seen @ 0.5 V

Synthesis of ^{13}C -enriched FEC

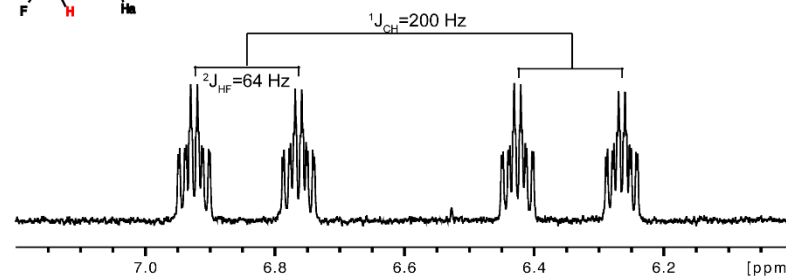
Based on the following prior literature:



G. Yao, Z. Dua, *Jingxi Huagong*, 29, 394-397 (2012).



^1H NMR of fully enriched product



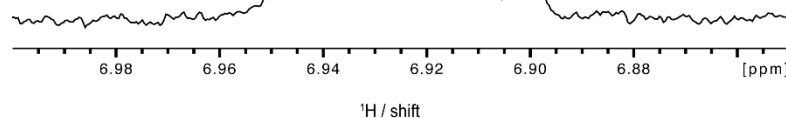
^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 6.43 (dddd, $J = 7.8, 6.9, 4.1, 1.0 \text{ Hz}$)

$^2J_{\text{CH}} = 7.8 \text{ Hz}$

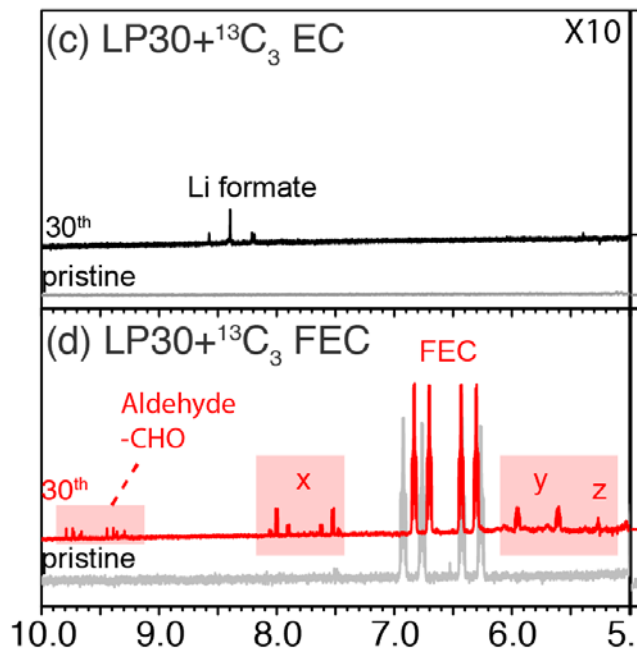
$^3J_{\text{HH}}(\text{cis}) = 6.9 \text{ Hz}$

$^3J_{\text{HH}}(\text{trans}) = 4.1 \text{ Hz}$

$^3J_{\text{CH}} = 1.0 \text{ Hz}$

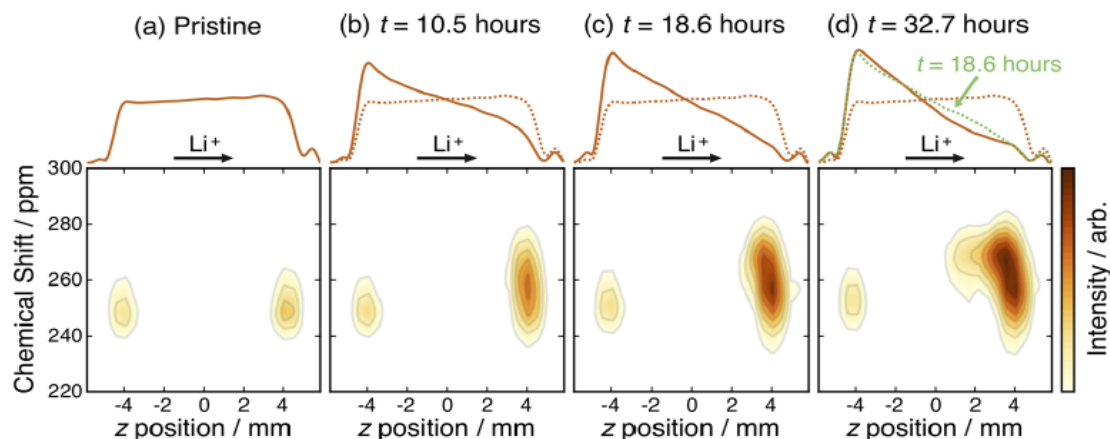
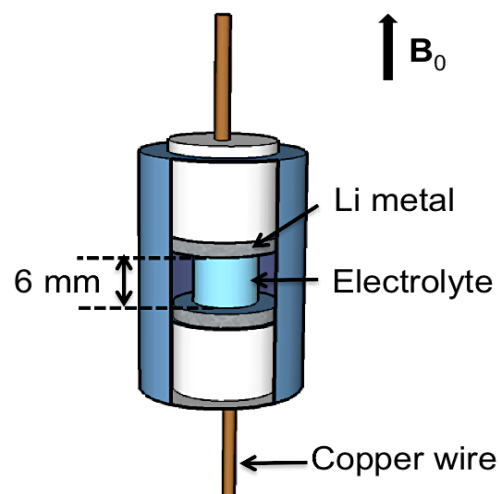


Analysis of the NMR spectra of the electrolyte (shown here after 30 cycles) shows evidence for VC and vinoxyl radical ($\text{O}=\text{C}-\text{CH}_2^\bullet$) derived species for FEC which are absent for EC only electrolytes



2. Metal Anode Dendrites: First study identified two regimes of dendrite growth

High current – moss to dendrite transition correlates with Sands time



Sands time $\tau_s = \pi D \left(\frac{C_0 e}{2J t_a} \right)^2$

C_0 = initial electrolyte concentration

t_a = transport no. of anion

J = Current density

D = ambipolar diffusion time

Lower current

Transition still occurs –

Sands time theory too

simple

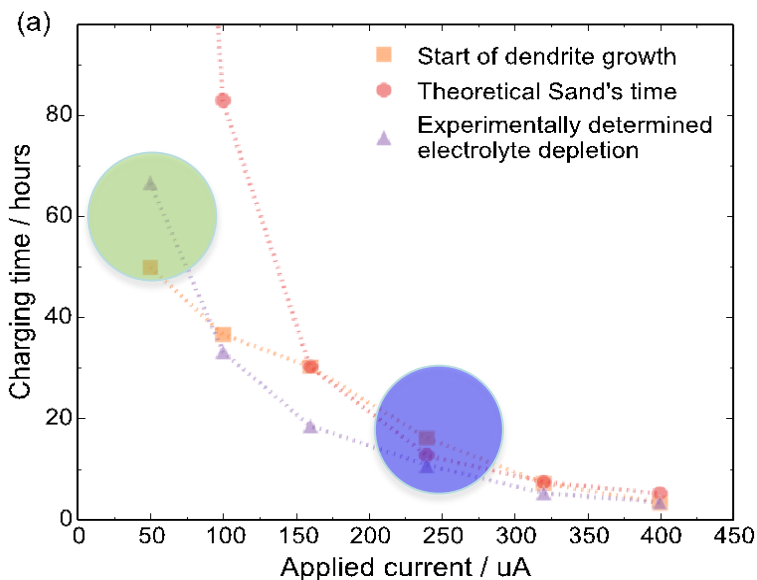
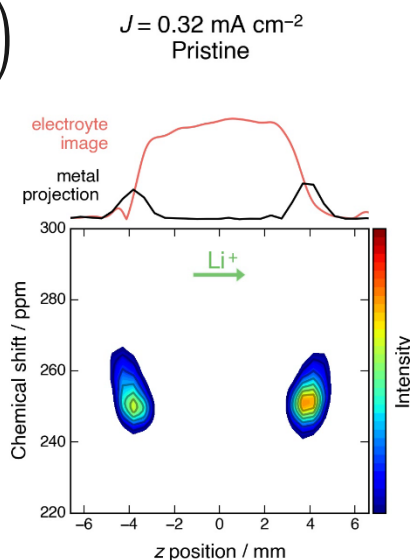
Role of SEI?

–Currently exploring

different additives,

electrolytes, salt

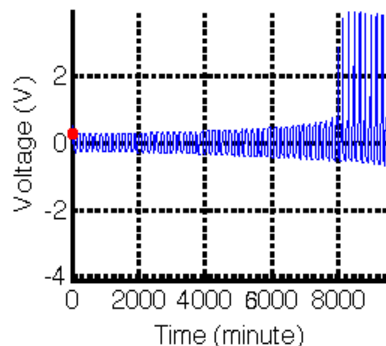
concentrations



Current also controls the nucleation vs. growth of dendrites: Application to Na anodes

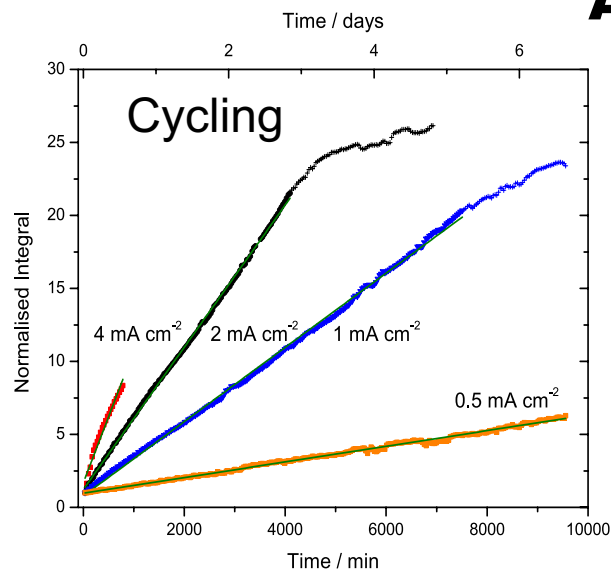
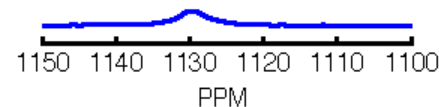
- High surface area deposits accumulate instantaneously

Current density
= 1 mA cm^{-2}

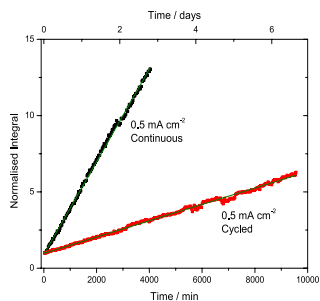


Quantify fraction of microstructure accumulation:

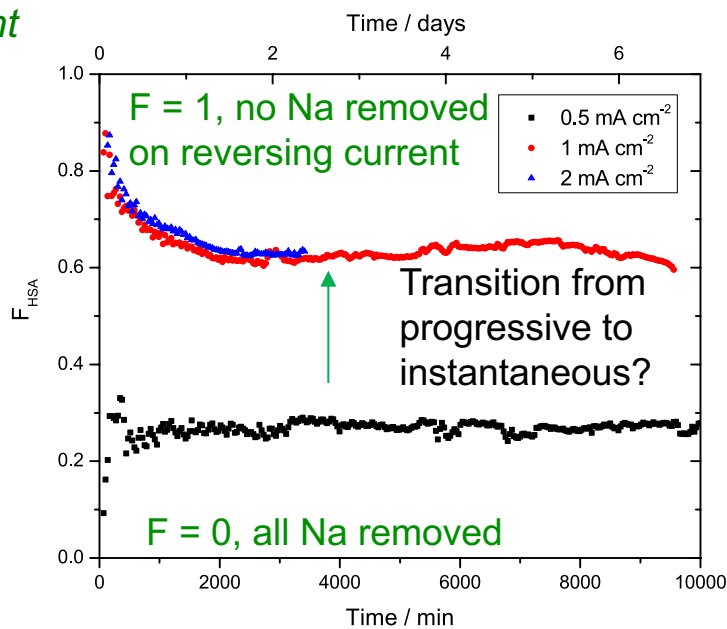
$$F_{HSA} = \frac{m_{NMR}}{m_{eChem}}$$



We are working in the low current regime



Rate / mA cm^{-2}	Slope (10^{-3}) Cycle vs. Const current	
0.5	0.5	3
1	2.5	7
2	4.9	12
4	9.0	



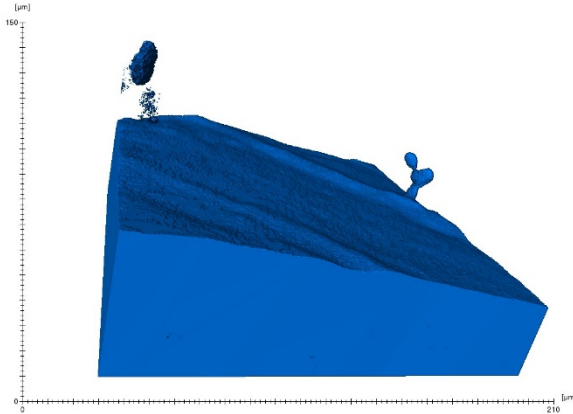
Deposition process governed by two (extreme) nucleation processes,
progressive
-the number of nucleation sites continues to grow with time,
instantaneous
-All nucleation sites are activated simultaneously.

Bayley, PM et al. *J. Am. Chem. Soc.* **2016**, 138, 1961.

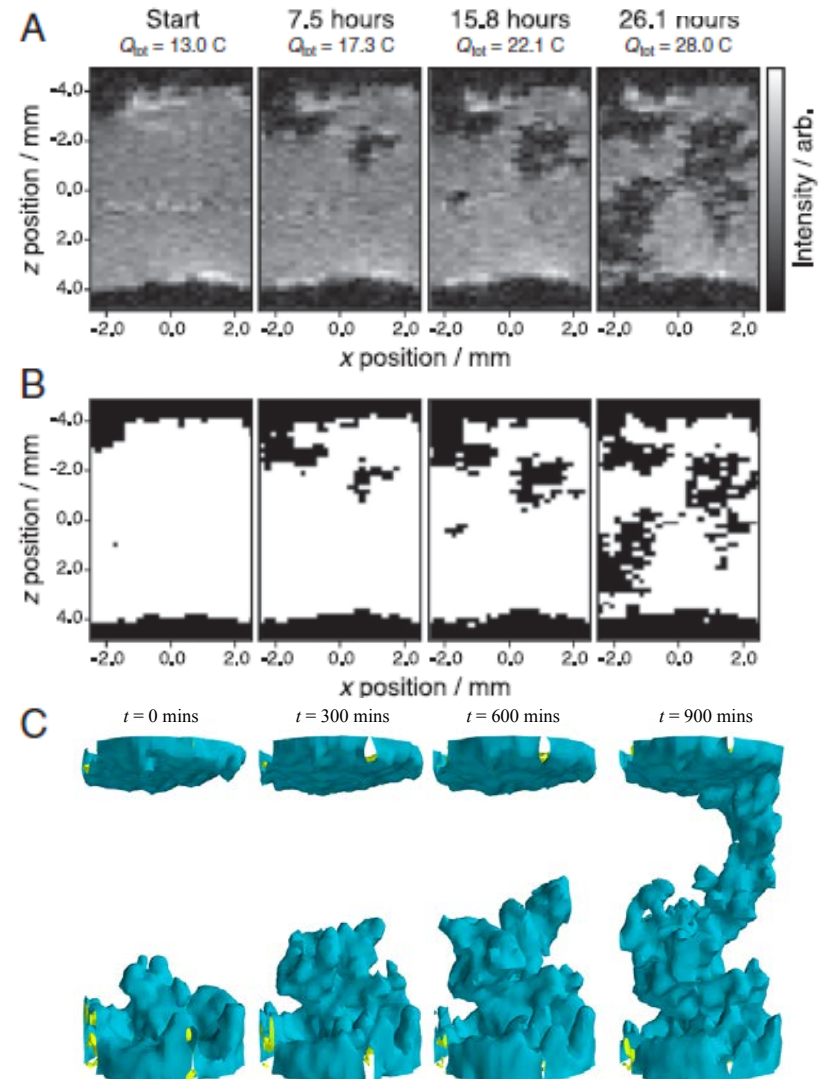
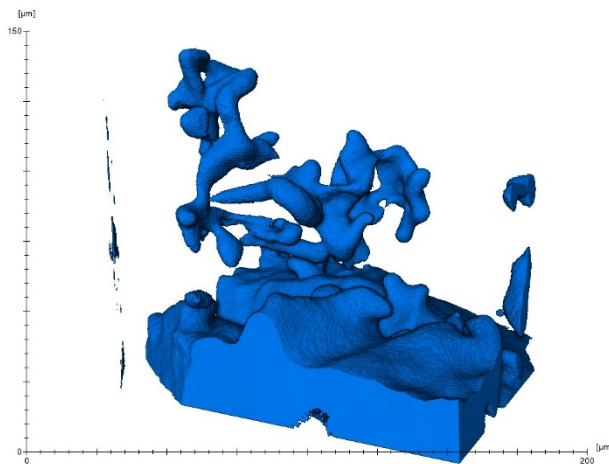
Imaging metallic microstructures with a combination of tomography and “Flash” MRI

¹H MRI

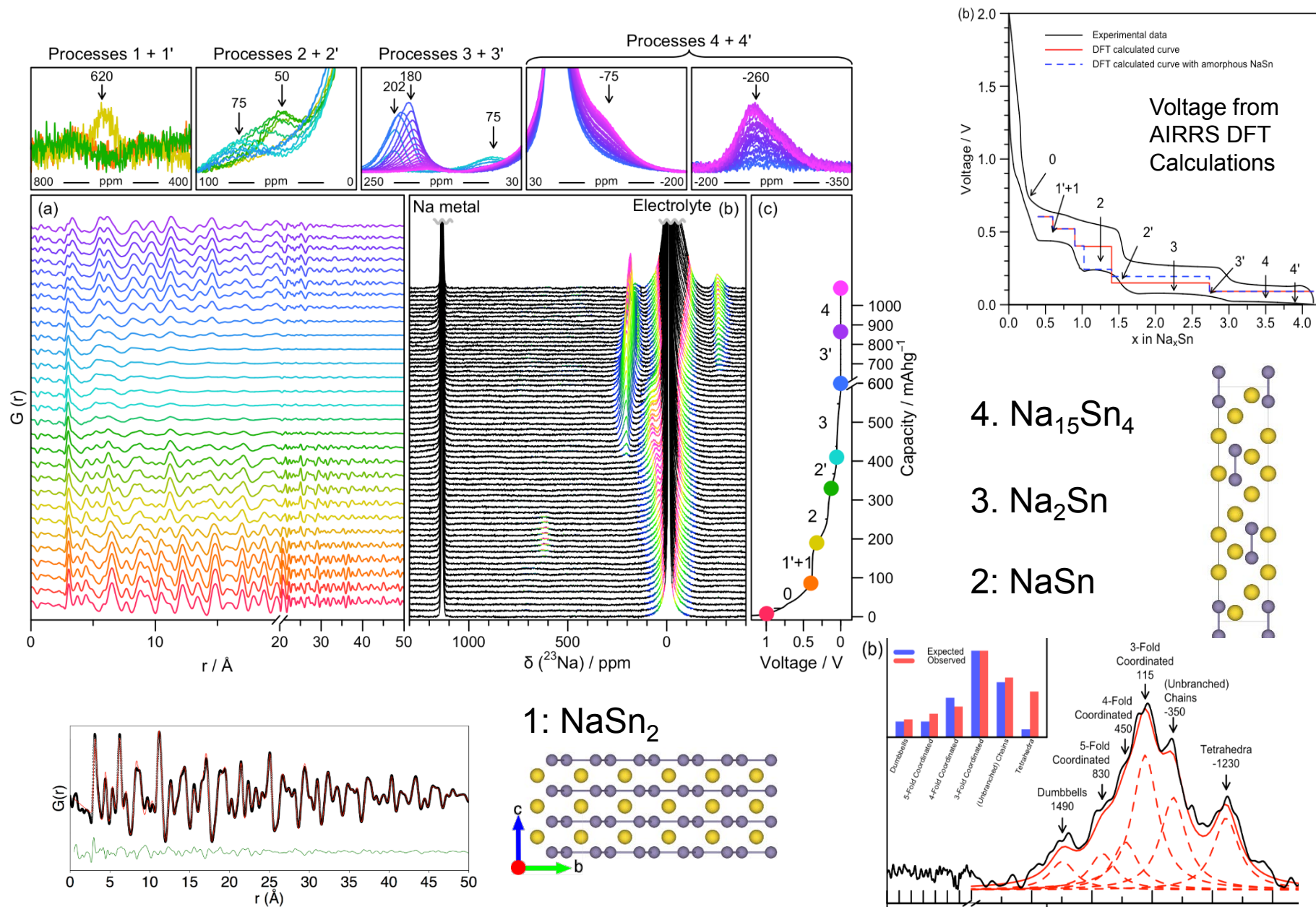
Initial nucleation event



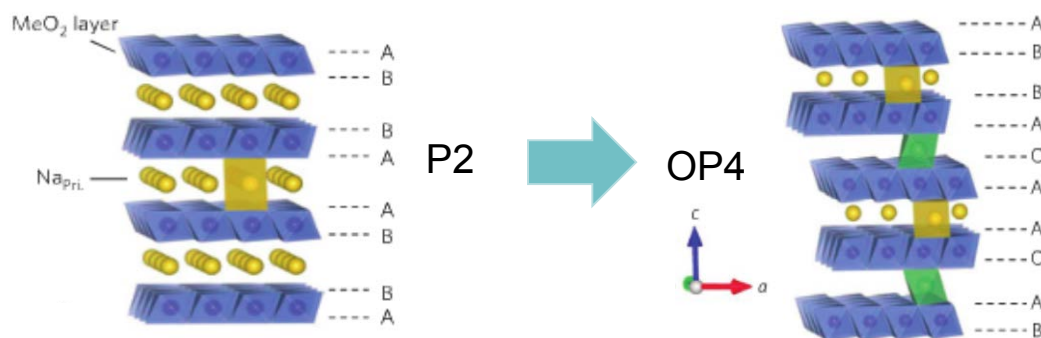
Final dendrites



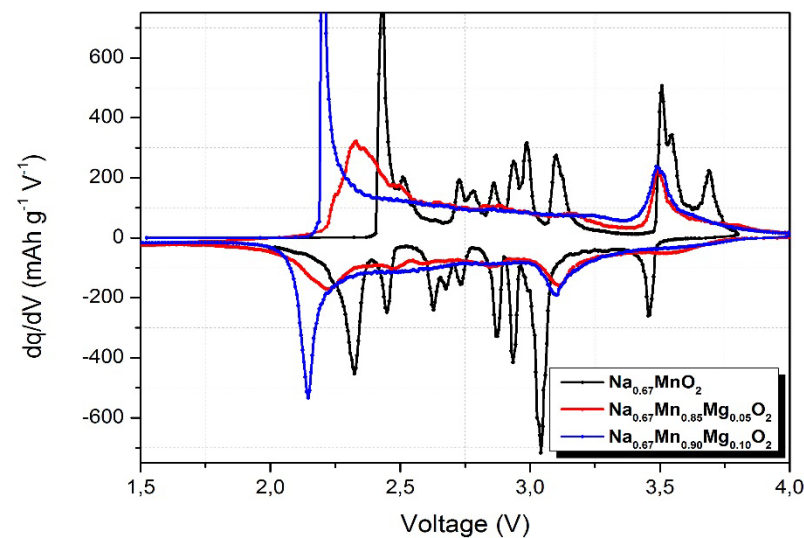
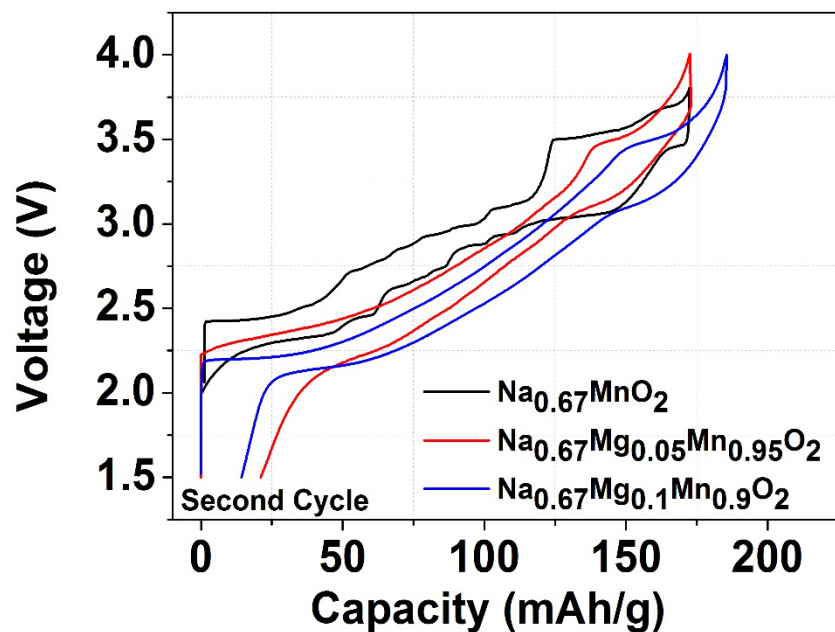
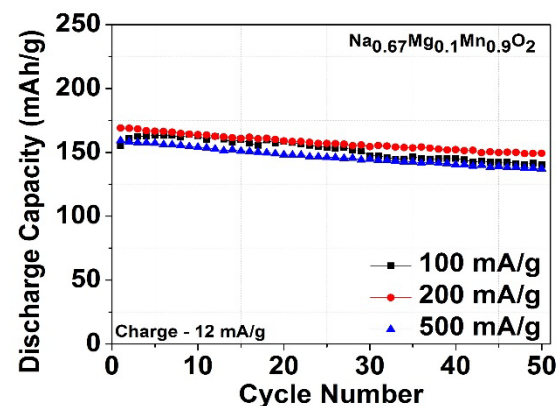
3. Na vs Li Electrodes: Operando ^{23}Na NMR and PDF Data Used to Solve the Structures of Crystalline Phases Formed For Na-Sn



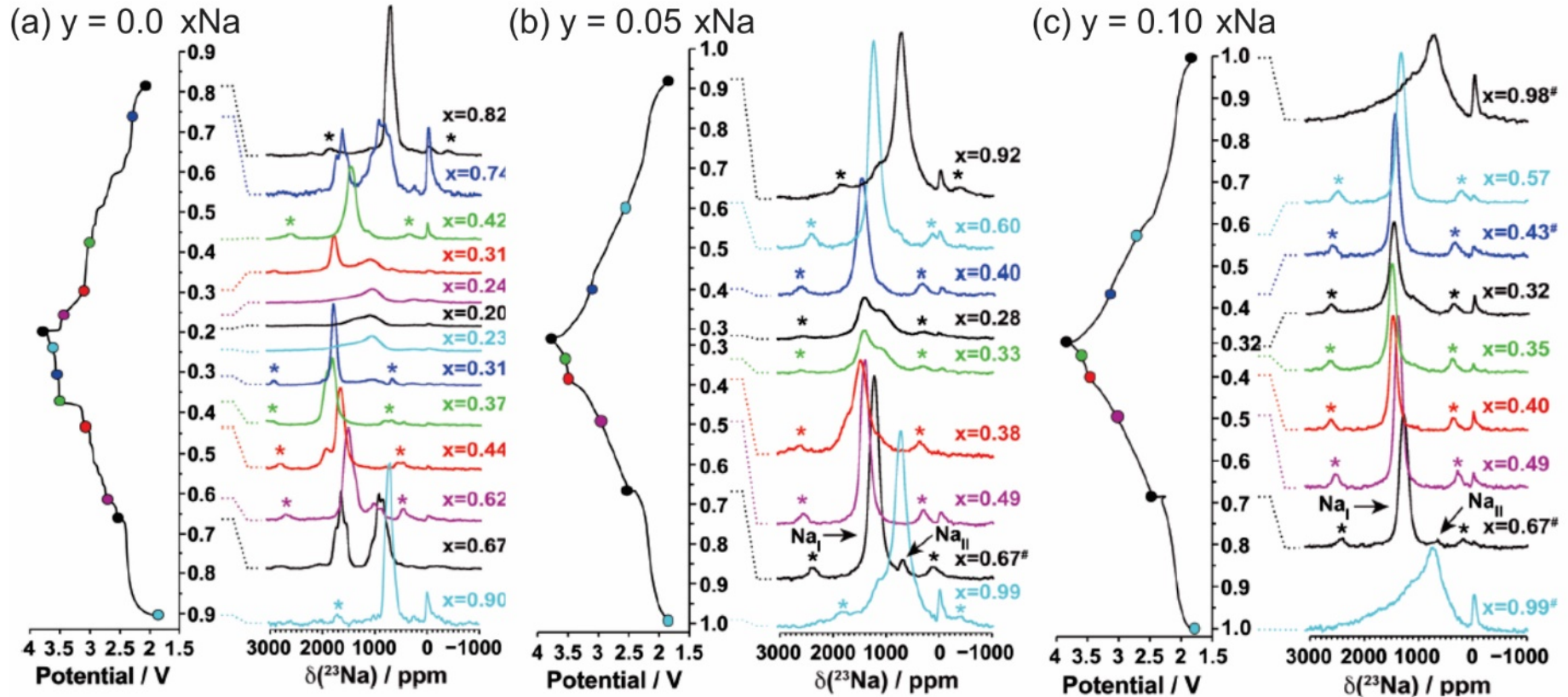
Using ^{23}Na NMR to Investigate Phase Transformations and Na Dynamics in Layered Na Cathodes: E.g., Mg-doped P2- $\text{Na}_{2/3}\text{MnO}_2$



Structural diagrams adapted from Yabuuchi et al., *Nat. Mater.* **11**(6) 2012

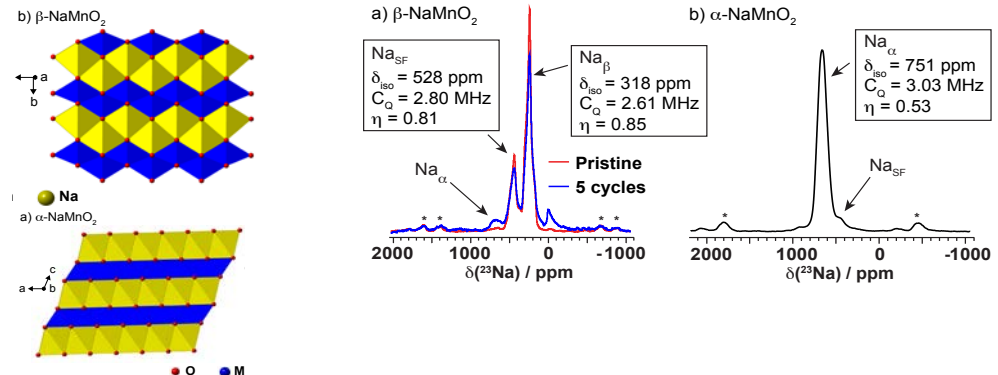


Ex situ solid-state ^{23}Na MAS NMR of $\text{Na}_{2/3}\text{Mn}_{1-y}\text{Mg}_y\text{O}_2$



- More gradual structural changes + less extensive OP4 phase formation when Mg present.
- Na mobility increased noticeably

Other studies include a study of stacking faults in $\beta\text{-NaMnO}_2$, and oxygen redox processes and Na mobility in Na layered phases $\text{P2-Na}_x[\text{Li}_y\text{Ni}_z\text{Mn}_{1-y-z}]\text{O}_2$ ($x, y, z \leq 1$)



Responses to Previous Year Reviewers' Comments

- Poster not reviewed last year

Collaboration and Coordination with Other Institutions

- Brett Lucht* (Rhode Island) – SEI and additives; provided reduced FEC/VC samples
- Jordi Cabana* (UIC); Stan Whittingham* (Binghamton), Shirley Meng*, Peter Bruce - Na cathodes (samples, magnetism)
- Stephan Hoffman, Cate Ducati, Andrew Morris (U. Cam) – Synthesis of Si nanowires, TEM, theory (Si)
- Dominic Wright, E. Eiser (U. Cam), new electrode coatings, ^{13}C -labeled FEC, EC
- Paul Shearing (UCL) – X-ray tomography
- *Chunmai Ban (NREL) – NMR characterization of alucone coatings

*BMR collaborators

Remaining Challenges and Barriers

- SEI studies are time consuming because the small sample sizes (poor S/N in NMR) and moisture/air sensitivity issues (cannot keep samples for long period of times).
comprehensive study takes time!
- Low yields for ^{13}C enriched FEC; limited access to DNP facilities
Continue to optimise yields and apply for DNP time
- MRI experiments limited by broken amplifier and need to redesign cell. Difficult to catch initial nucleating process.
Have now built relevant e-chem cells for MRI.

Proposed Future Work

- Complete/write up DNP of ^{13}C -labeled electrolyte/additive on Si SEI study
- Complete/write up ^{13}C -enriched FEC Si SEI study
- Continue Si-coating studies – currently studying all inorganic, hybrid-inorganic/organic coatings
- Investigate SEI in presence of coatings
- Develop new NMR methods for determining sizes and intermixing (distances between) different components in the SEI
- Investigate effect of additives and different electrolytes (e.g. ionic liquids) on Li dendrite growth via NMR, MRI and tomography
- Characterize SEI formed in NMR/MRI studies by XPS and SIMS to help interpret NMR/MRI results
- Continue to investigate Na-ion negative electrodes – complete Sn and compare with hard carbons and phosphides.
- Start work on Na SEI

Any proposed future work is subject to change based on funding levels

Summary

Silicon SEI:

- FEC and VC were directly reduced with LiNap to analyze decomposition products with ssNMR, XPS, FTIR, and MS to understand the composition of Si SEI
- Both FEC and VC form poly(VC) albeit in different quantities.
- ^{13}C -labeled EC and FEC have been synthesized and ssNMR and DNP experiments have been performed
- Preliminary DNP experiments indicate that cycled Si electrodes with FEC show evidence of formation of poly(VC), consistent with findings of direct chemical reduction study
- Analysis of soluble products formed on cycling Si nanowires with FEC enriched electrolytes show the formation of VC derived products and species originating from vinoxyl radicals.

Li Dendrites:

- Two mechanisms for microstructure growth clearly seen: mossy and dendritic
- With a more robust understanding and control of SEI composition, we can leverage this information to learn how SEI influences Li microstructural growth
- How does changing the electrolyte composition change Li dendrite growth? How do ionic liquids change SEI/dendrite growth?
- Imaging in high resolution: ^1H FLASH MRI in conjunction with tomography techniques

Beyond Li:

- Na metal microstructures continuously plate and grow more readily than Li.
- Transition from progressive nucleation and growth to instantaneous nucleation and growth on increasing the current
- Transition metal doping (e.g. Mg) can be used to increase Na mobility in paramagnetic cathode materials for Na ion batteries
- PDF and NMR methods in combination with theory can be used to solve the structures formed on sodiating Sn anodes. New layered Sn phase discovered.

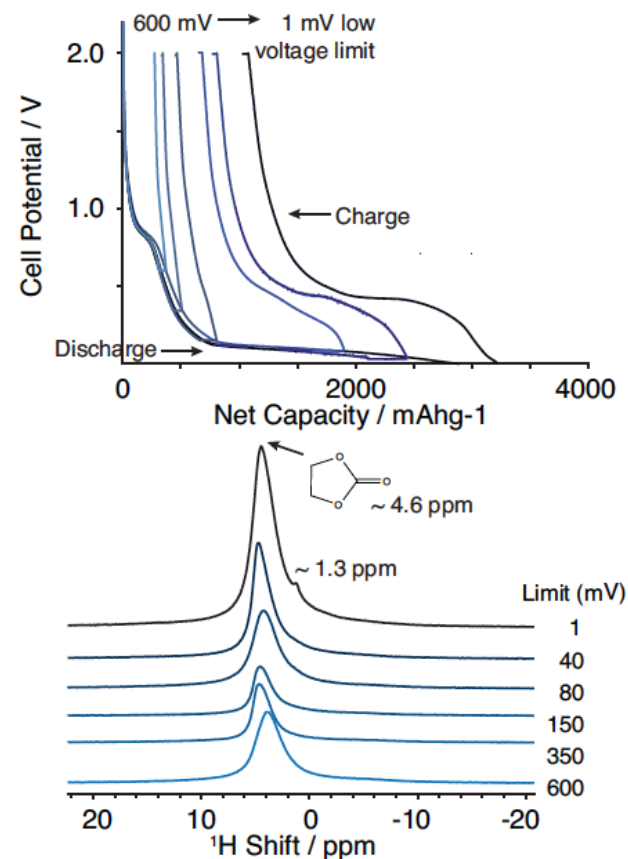
Technical Back-Up Slides

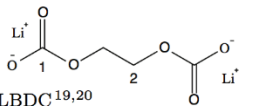
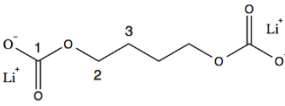
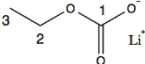
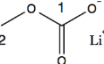
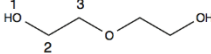
1. Silicon SEI with EC/DMC only

First Studies Used Binder Free System – to remove ^{13}C background and produce *more* SEI

Voltage Dependent
Composition of the SEI:

Use DFT Methods to Provide Estimates for
 $^{13}\text{C}/^1\text{H}/^7\text{Li}$ NMR Shifts of Predicted Products and
Functional Groups:



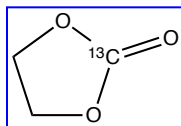
Molecule	Atom	Calculated and Measured Chemical Shifts / ppm		
		ChemNMR	DFT	Experimental
LEDC				(solvent: AC-d ₆ ⁹ /D ₂ O ⁷)
	C1	161	171.0	157/161.2
	C2	65.5	64.5	62.9/62.5
	H2	4.39	4.3	3.53/3.51
	Li	-	0.9	
LBDC ^{19,20}				
	C1	161	171.3	
	C2	67.1	68.0	
	C3	24.8	25.4	
	H2	4.21	4.1	
	H3	1.61	1.7	
	Li	-	1.0	
LEC				
	C1	161	171.4	163.7
	C2	63.5	62.8	60.1
	C3	13.8	11.9	19.4
	H2	4.21	4.1	3.65
	H3	1.27	1.5	1.17
	Li	-	1.0	
LMC				(solvent: AC-d ₆ /DMSO ⁹ /D ₂ O ⁸)
	C1	161	171.9	160.97/157.02/163
	C2	54.1	51.5	62.40/51.51/54.6
	H2	3.68	3.8	3.56/3.27/3.35
	Li	-	0.9	na
PEO				
	C2	61.3	62.5	
	C3	70.3	70.9	
	H1	5.4	0.1	
	H2	3.7	4.0	
	H3	3.54	3.7	

^1H NMR: New species at 1.3 ppm (saturated CH groups) emerges at lower voltages

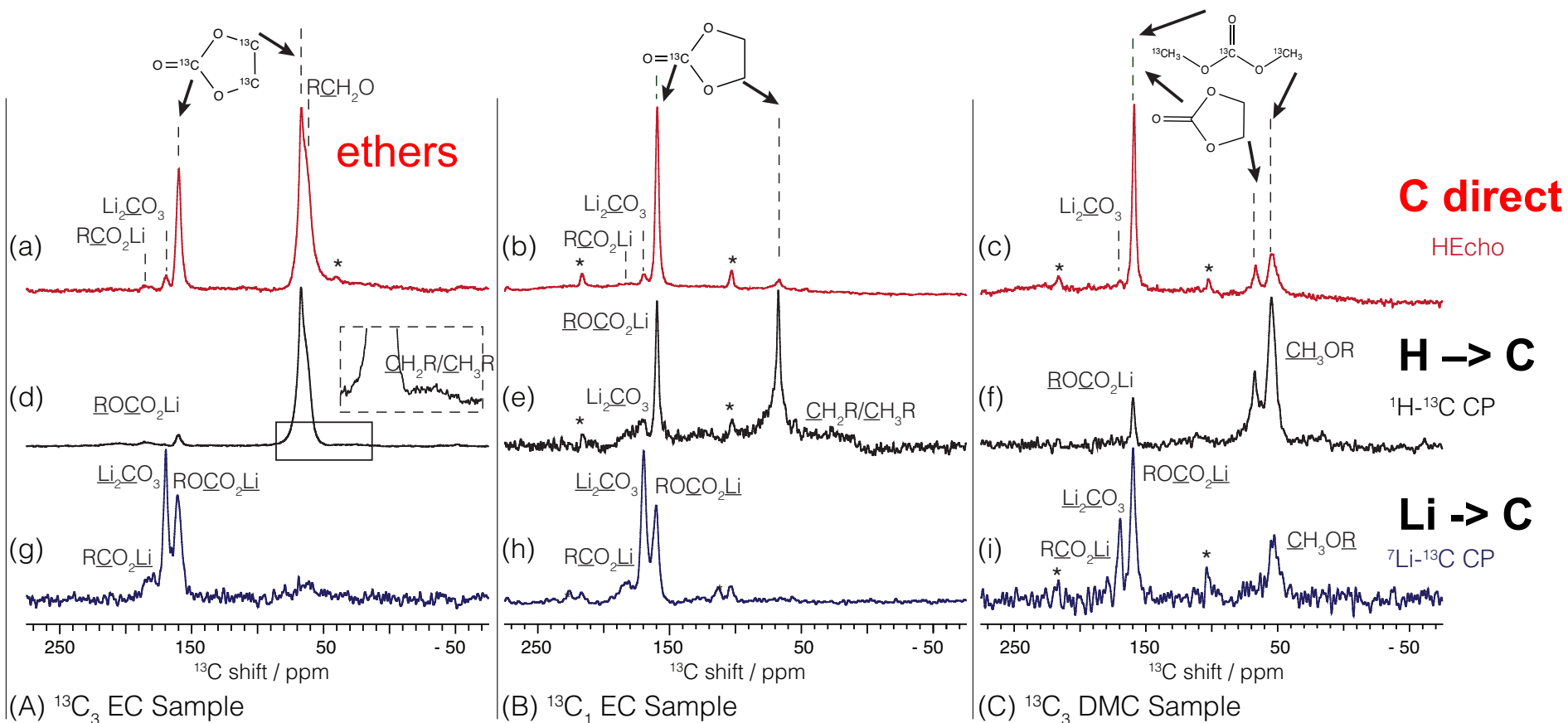
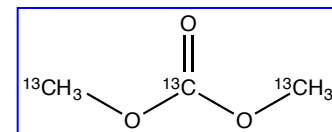
Composition of the SEI on Silicon after 1 cycle

- Detailed ^{13}C measurements of selectively labeled molecules yield composition of organics
High concentration of EC trapped in SEI
- Li- \rightarrow C CP detects lithiated carbonates (ROCO_2^-), Li_2CO_3 , formates (H- and RCO_2Li)
- A number of ether carbons from EC/DMC decomposition products are detected beneath the EC resonances

^{13}C -enriched EC

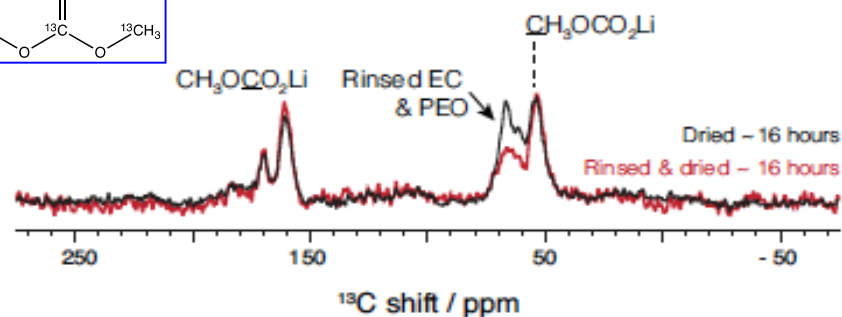
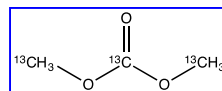
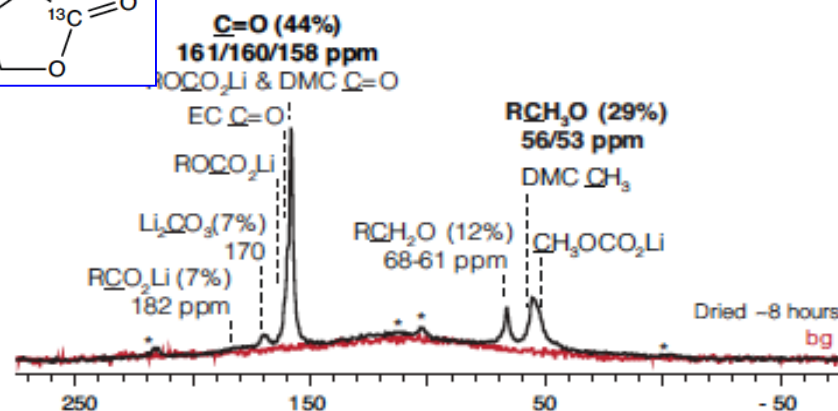
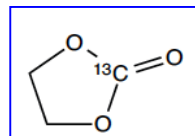
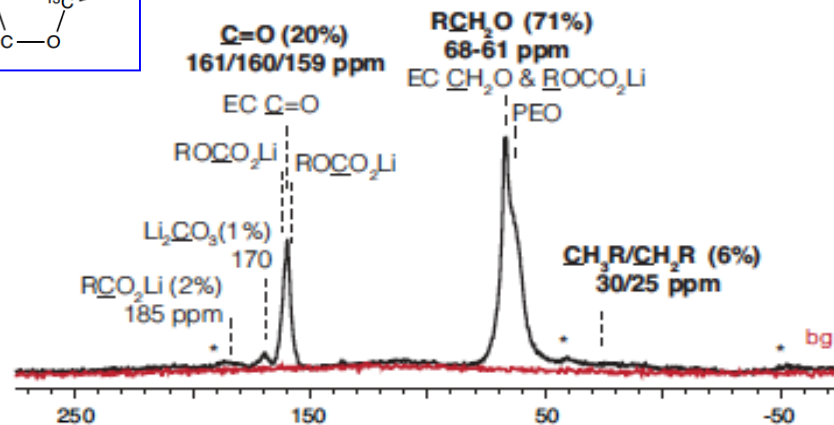
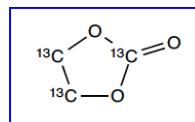


DMC



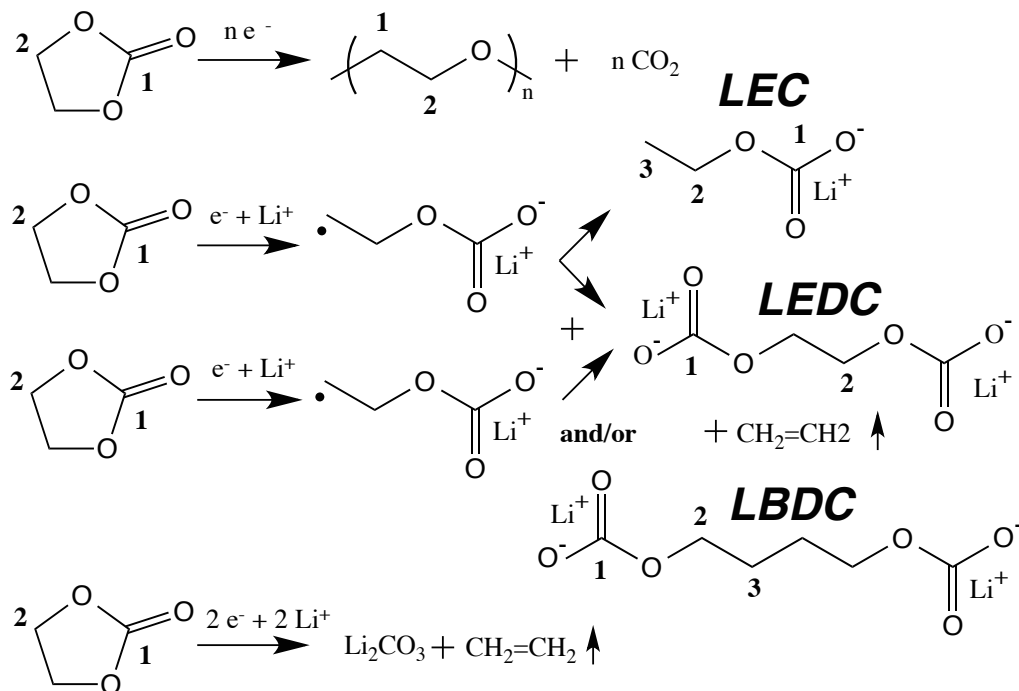
Quantification of the signals/species

Proposed Decomposition Products	Total ^{13}C Signal (%)	Molecular Ratio
(a) $^{13}\text{C}_3$ EC Sample		
PEO $-\text{OCH}_2\text{CH}_2\text{O}-$	51	25
LEDC $(\text{CH}_2\text{OC}_2\text{Li})_2$	28	7
LEC $\text{CH}_3\text{CH}_2\text{OCO}_2\text{Li}$ and LBDC $(\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li})_2$	18	6
RCO_2Li	2	2
Li_2CO_3	1	1
(b) $^{13}\text{C}_3$ DMC Sample		
LMC $\text{CH}_3\text{OCO}_2\text{Li}$	58	29
Non-labelled EC and products	27	
RCO_2Li	7	7
Li_2CO_3	7	7



Proposed Decomposition Mechanisms of EC & DMC

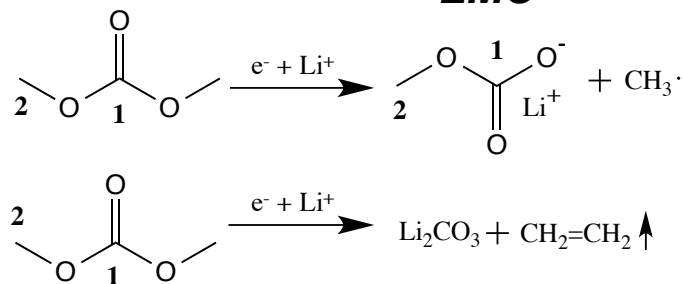
PEO



Our results showed experimental evidence of decomposition products, consistent with theoretically predicted reduction mechanisms.

LEDC is widely believed to be an important EC decomposition product. We also observe evidence for LBDC and LEC ($\text{CH}_2\text{R}/\text{CH}_3\text{R} \sim 30/25 \text{ ppm, C3}$).

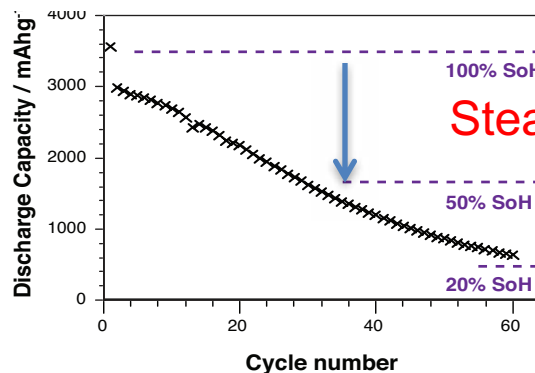
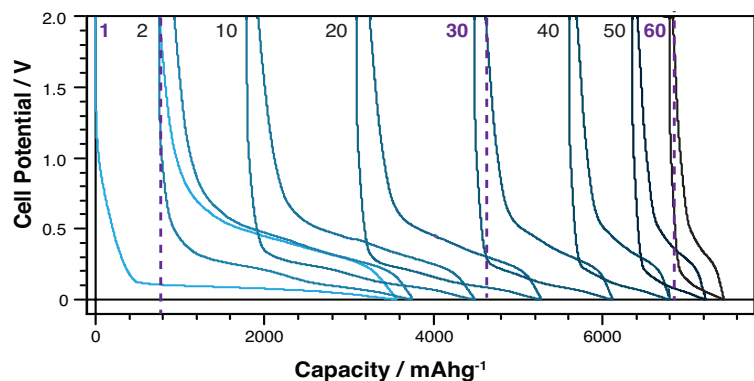
LMC



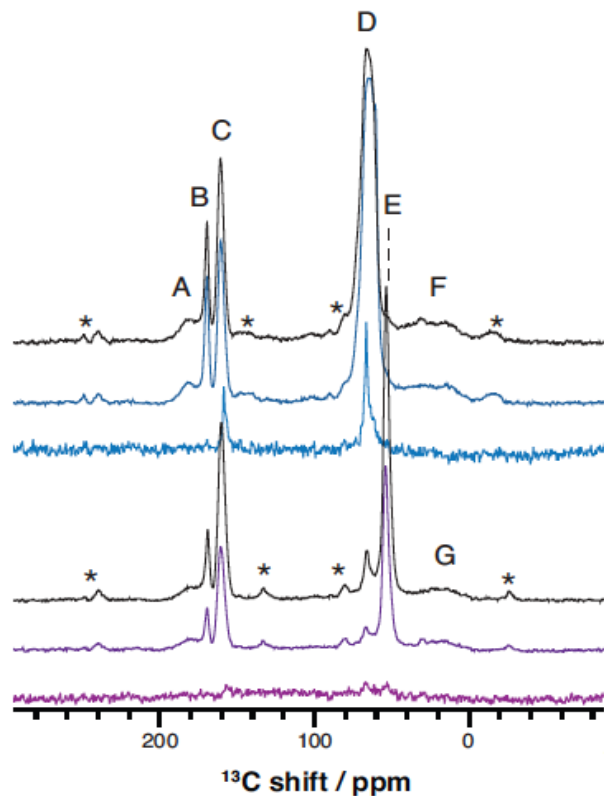
Note that:

- some $\text{CH}_2(\text{or } \text{CH}_3)\text{CH}_2\text{-O}$ comes from DMC reactions *not* described above
- ^1H NMR suggest that these species are formed during the low V plateau

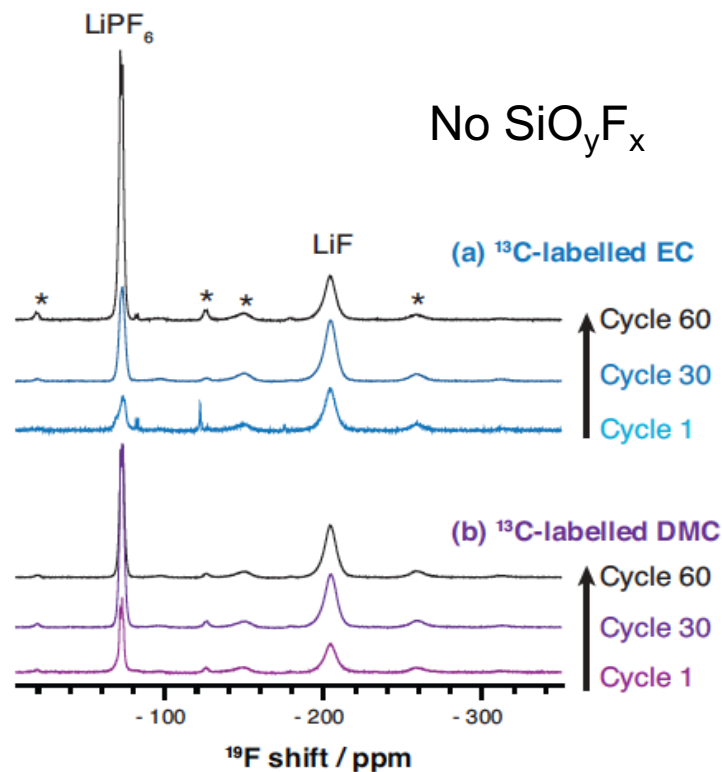
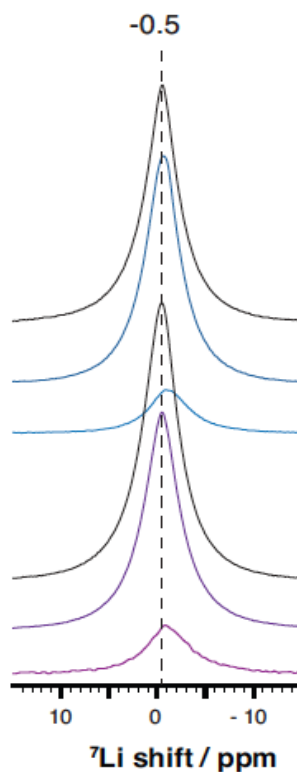
“Extended” cycling with CMC



No distinct difference seen by NMR



Minor organics on 1st cycle

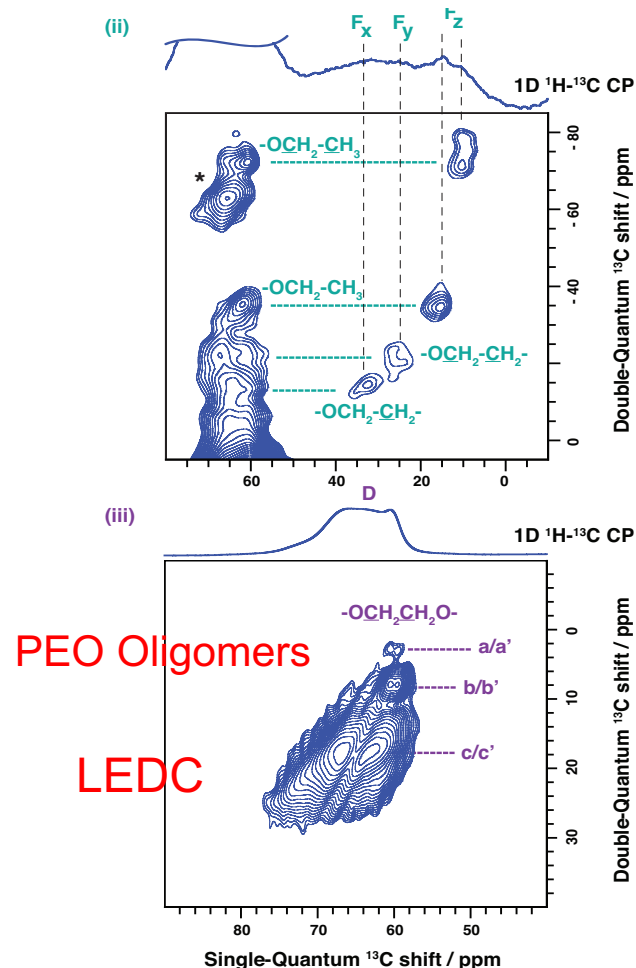
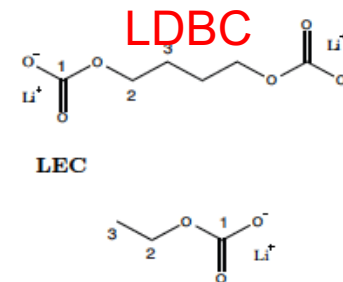
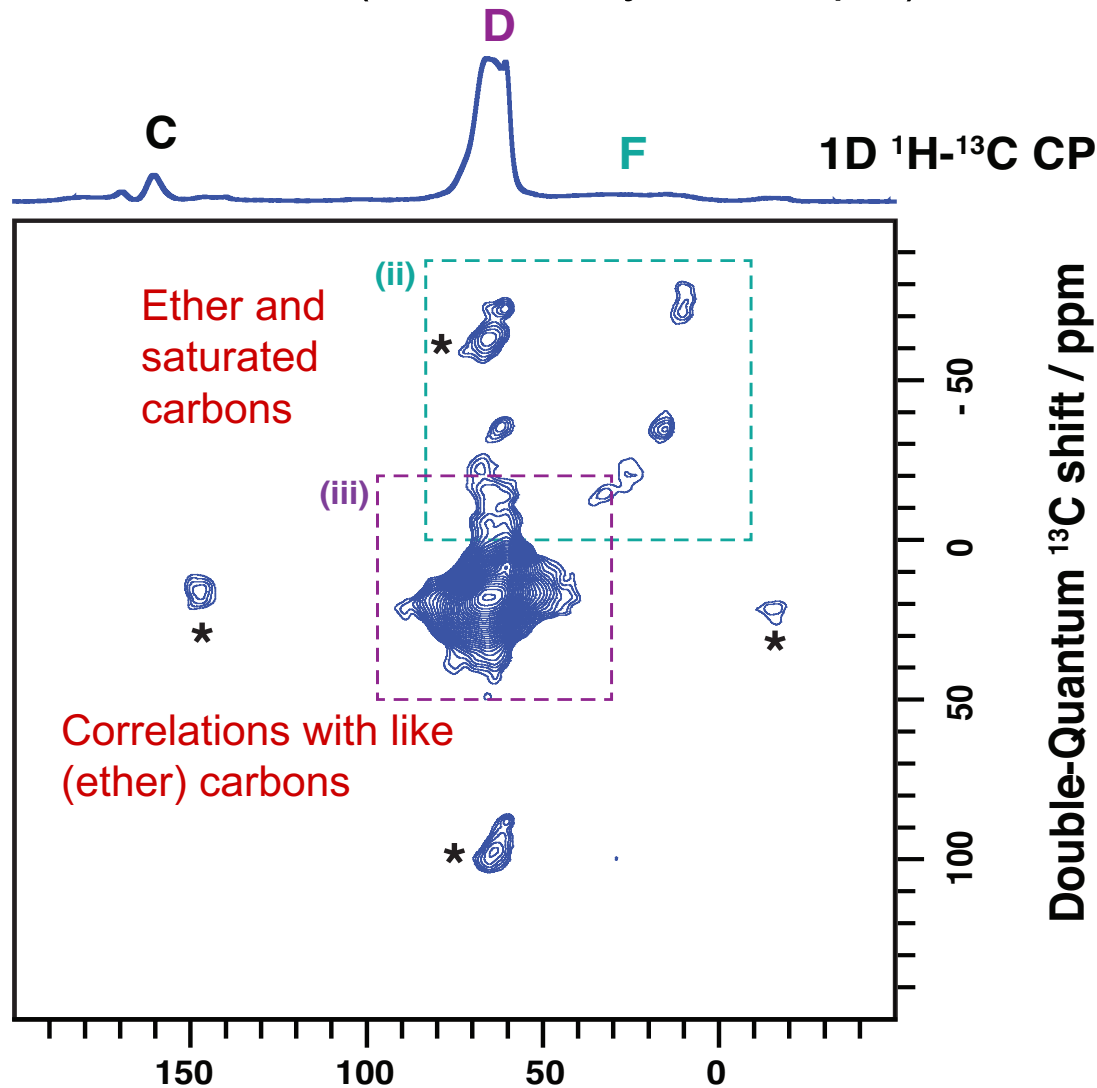


Significant LiF on 1st cycle

No SiO_yF_x

Identification of longer chain organics

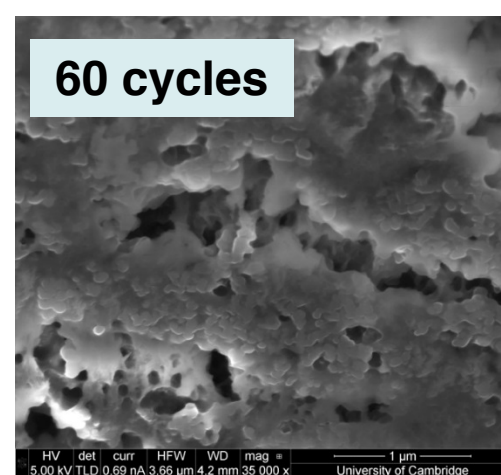
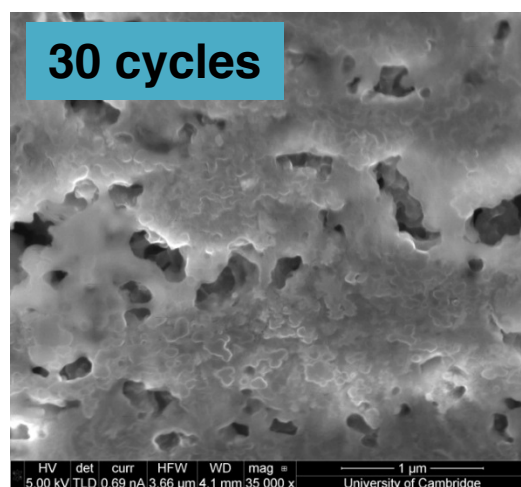
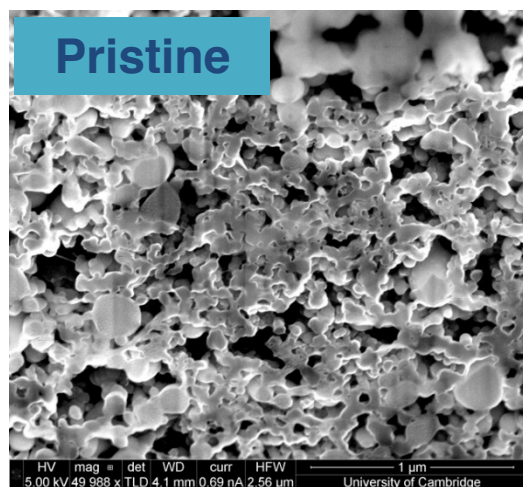
2D correlations between **bonded carbon atoms**
(CMC, 15 cycle sample)



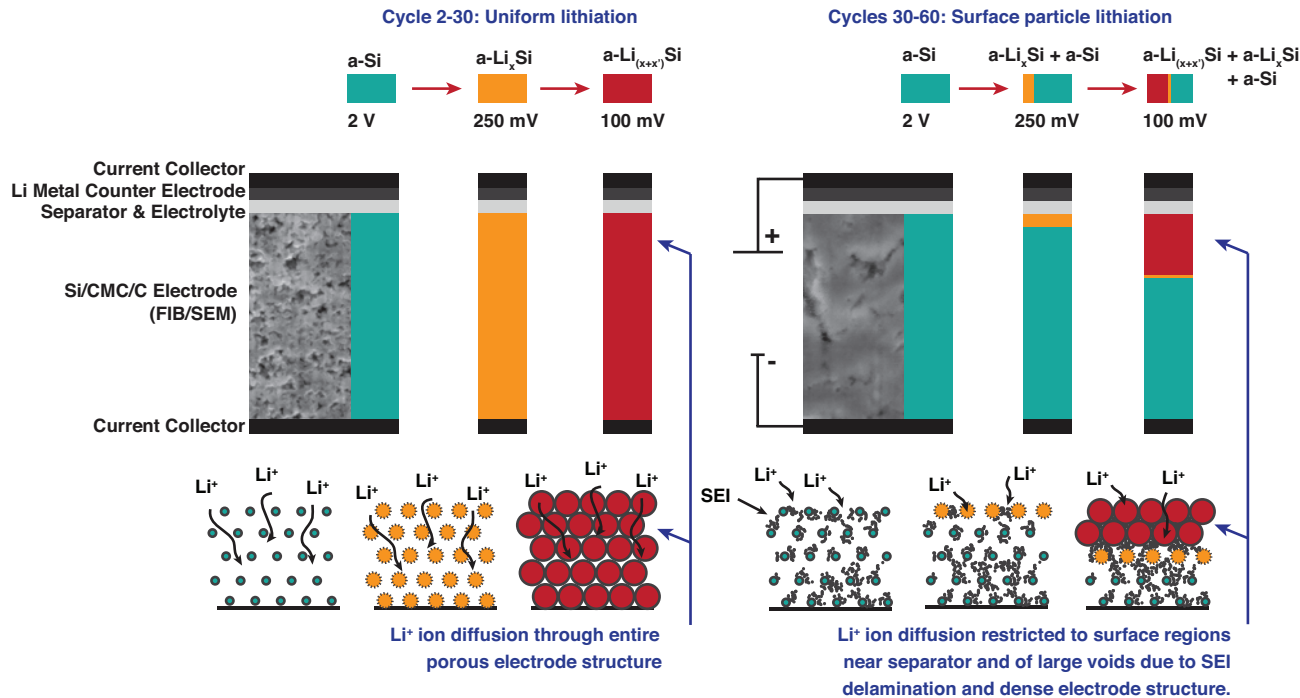
Identification of longer chain organics

Resonance	^{13}C Shift/ppm	Fragment
A: EC/DMC	179	$\text{R}\underline{\text{C}}\text{O}_2\text{Li}$, $\text{H}\underline{\text{C}}\text{O}_2\text{Li}/\text{CH}_3\text{CH}_2\underline{\text{C}}\text{O}_2\text{Li}$
B: EC/DMC	170	$\text{Li}_2\underline{\text{C}}\text{O}_3$
C: EC/DMC	160	$\text{RO}\underline{\text{C}}\text{O}_2\text{Li}$, residual EC/DMC $\underline{\text{C}}=\text{O}$
D: EC/DMC	67	$\underline{\text{R}}\text{OCO}_2\text{Li}$, residual EC $\underline{\text{C}}\text{H}_2$, PEO $-\text{O}\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_2\text{O}-$
E: DMC	53	CH_3OLi residual DMC CH_3
F_x : EC	30	$\text{R}\underline{\text{C}}\text{H}_2\text{R}'$
F_y : EC	23	$\text{CH}_3\underline{\text{C}}\text{H}_2\text{R}$
F_z : EC	14	$\underline{\text{C}}\text{H}_3\text{R}$
G_x : DMC	30	$\text{R}\underline{\text{C}}\text{H}_2\text{R}'$
G_y : DMC	23	$\text{CH}_3\underline{\text{C}}\text{H}_2\text{R}$
G_z : DMC	14	$\underline{\text{C}}\text{H}_3\text{R}$

Assignments for the ^{13}C spectra of the 15 cycle sample

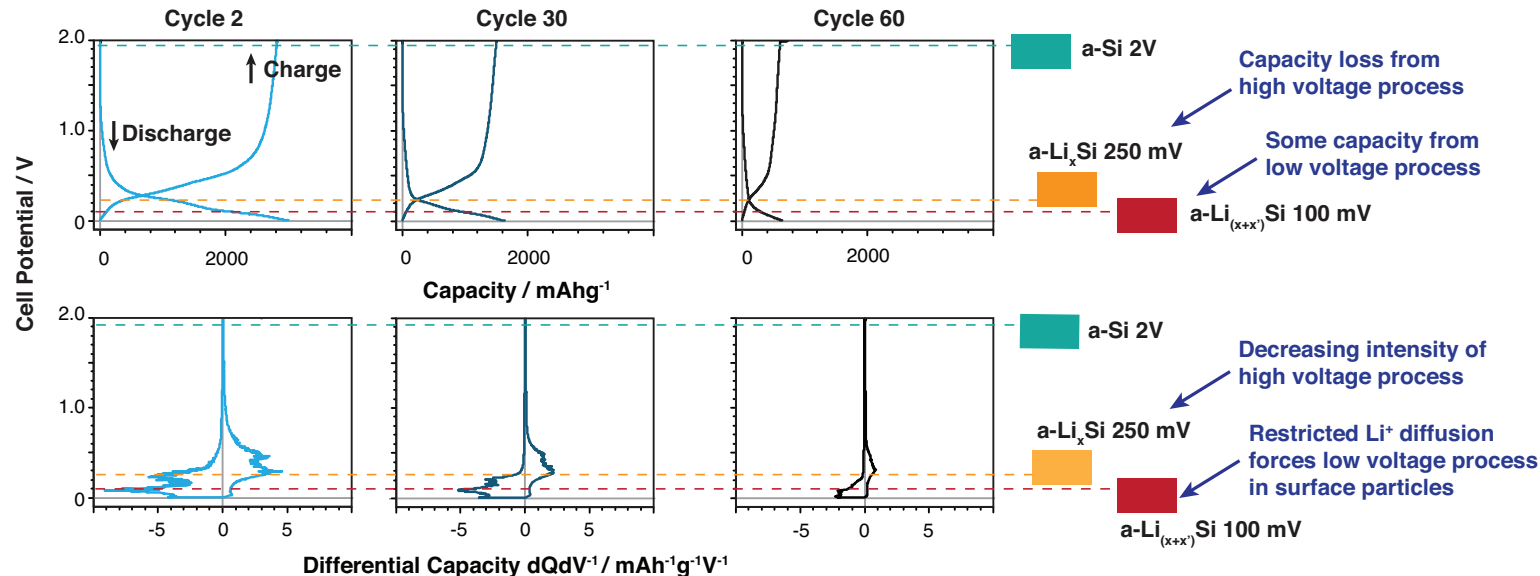


Cycling with CMC

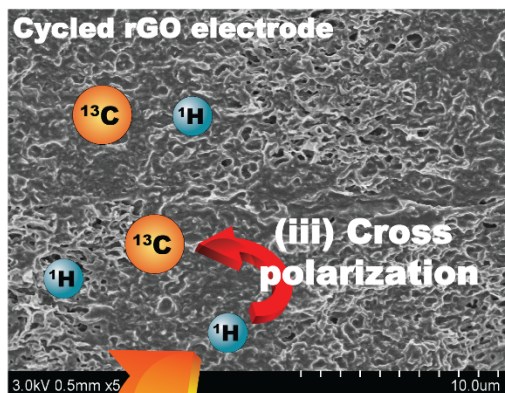
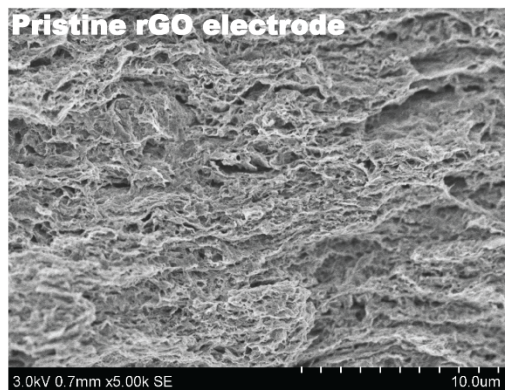


Li^+ ion diffusion in the increasingly dense electrode structure: expansion on lithiation reduces transport through top of electrode

Capacity loss and evolving kinetics: high voltage process lost due to increased tortuosity through electrode



DNP MAS NMR – enhanced sensitivity of organic SEIs on cycled rGO electrode

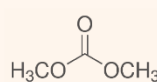


ELECTROCHEMICAL CYCLING

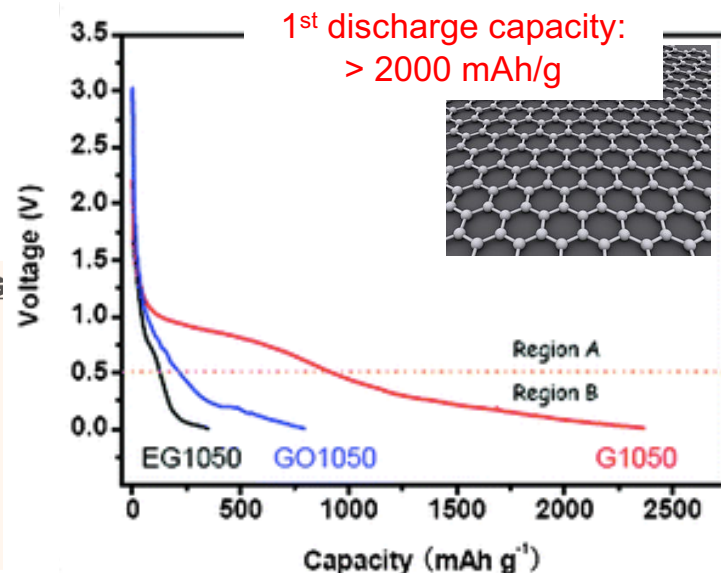
Reduced GO cycled with
1M LiPF₆ in EC/DMC,
against Li metal,
with C rate of 50 mA/g



EC

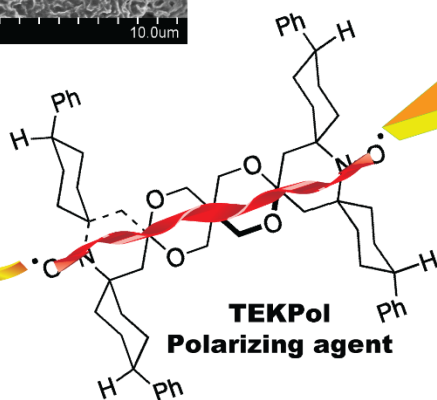


DMC



Graphene*

**(ii) Transferring
e⁻ polarization
to solvent
via cross effect**



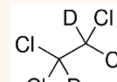
(i) MICROWAVE

DNP SAMPLE PREPARATION

Cycled rGO electrode (~7 mg)
mixed with 7 μL of 16mM TEKPol
in TCE/TCE-d₂/CDCl₃ solution



**TCE
56**

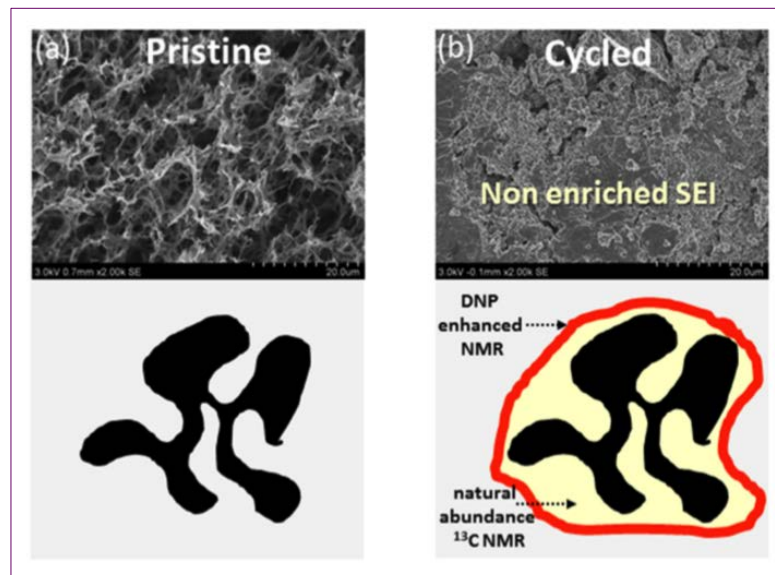
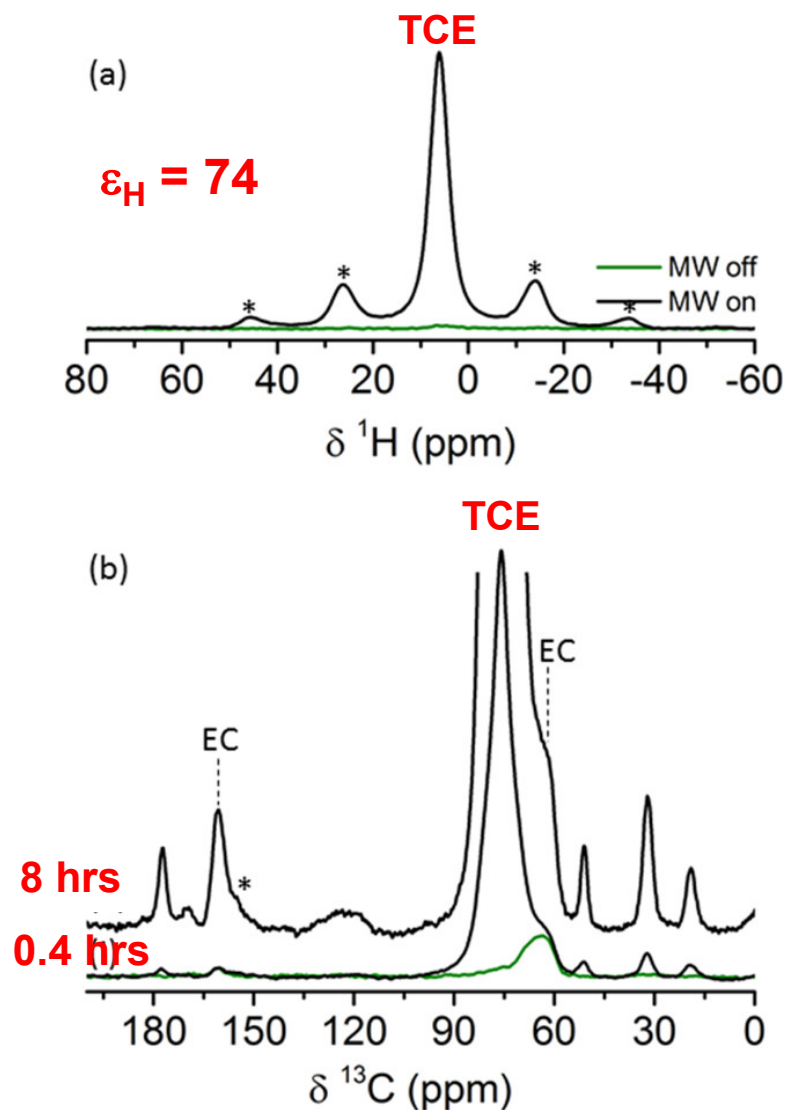


**TCE-d₂
24**



**CDCl₃
20**

DNP MAS NMR – enhanced sensitivity from organic SEIs on cycled rGO electrode (cont'd)



- Detecting SEIs with natural abundance (NA) ^{13}C electrolyte by ssNMR is beyond sensitivity limit
- Enhanced sensitivity and resolution from a cell cycled with NA ^{13}C electrolyte by DNP in a reasonable time
- New approach to study the surface layers formed in many electrode materials